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BINDING OF URANYL BY HUMIC ACID

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Abstract—The binding of tracer level UO_2^{+2} to a soil humic acid was measured by a solvent extraction technique The binding is interpreted as involving only the carboxylate groups of the humate and both 1 1 and 1 2 UO_2^{+2} CO_2^- binding is observed Estimates based on these values indicate that uranyl complexing by humic and/or fulvic materials is not significant in sea water but may play a role in fresh water systems Retention of uranyl from ground water by soil humics would be strong

INTRODUCTION

Studies of the interaction of Ca(II), Am(III), and Th(IV) with humic acids have been reported previously from this laboratory[1–4] In this paper we report the results of investigations of the binding of uranyl ion, UO_2^{+2}, to humic acid Uranyl interaction with humic material is interesting *per se* as a probable mechanism for the accumulation of uranium in natural deposits[5, 6] In addition, UO_2^{+2} is a close chemical analog of PuO_2^{+2} but is more resistant to reduction Consequently, the behavior of UO_2^{+2} is a valid model for that of PuO_2^{+2} in the absence of reduction of the latter upon interaction with humate Knowledge of plutonium ecology is of direct importance in connection with problems of nuclear power involving deliberate and accidental releases to the environment

EXPERIMENTAL

Reagents Di(2-ethyhexyl) phosphoric acid, HDEHP used in the solvent extraction studies was obtained from Pfaltz and the Bauer, Inc , and purified by a modification[7] of the method of Peppard *et al* [8] Technical grade humic acid from Aldrich Chemical Company was purified as described previously[2 3] to an ash content of 2–3% The other chemicals used were reagent grade and required no additional purification

Uranium–233 of high specific activity was obtained from Oak Ridge National Laboratory It was purified by passage through a bed of anion exchange resin using 8 M HCl solution as eluant Counting of the ^{233}U radioactivity was performed with a Packard Model 332 liquid scintillation counter using an extractant scintillation counter using an extractant scintillation cocktail of 6 g/l HDEHP and 6 g/l PPO in toluene which had been purified by passage through a column of alumina

Procedures (a) The humic acid was evaluated by pH titration for its cation exchange capacity and its acid constant In a typical experiment 10 ml of a solution containing 2 g/l of humic acid in 0 09 M $NaClO_4$ + 0 01 M NaOAc was titrated with a solution of 0 09 M $NaClO_4$ + 0 01 M NaOH (b) To measure the binding constants, 10 ml of humic acid solutions of a known pH (using glycolate buffer) and a constant ionic strength of 0 10 M [$(Na^+ + H^+) + (ClO_4^- + Gl^-)$] were contacted with 10 ml of HDEHP solution in toluene Approx 0 01 μCi of ^{233}U was added to the mixture which was sealed in a vial and rotated in a constant temperature bath for at least 20 hr The aqueous and organic phases were equilibrated with the appropriate counter phase just prior to use in the extraction experiments After a rotation time sufficient to ensure equilibrium, the two phases were allowed to separate A portion of each phase was removed and centrifuged and duplicate 0 50 ml aliquots taken for counting These were added to the extractant scintillation cocktail, the pH adjusted to 3 and the mixture shaken The samples were counted to an error of ±1% The pH of the aqueous phase after equilibration was determined using a combination electrode and a Beckman Research pH meter

RESULTS

From the base titration of the humate–acetate solution, it was determined that humic acid had 4 2 meq/g of ionizable acid groups Further, these carboxylate sites were found to have a pK_a value of 4 19 ± 0 06 at 50% ionization

A study of the variation of the log of the extraction constant for uranyl tracer as a function of solution pH between pH 1 85 and 2 75 gave a dependence of 2 01 ± 0 01 Similarly, uranyl extraction by HDEHP was shown to have a second power dependence on $[(HDEHP)_2]_o$ Therefore, the extraction equation can be written

$$UO^{+2}_{2(aq)} + 2(HDEHP)_{2(o)} = UO_2[(DEHP)(HDEHP)]_{2(o)} + 2H^+_{(aq)} \qquad (1)$$

with an extraction constant defined as

$$D_o = \frac{(UO_2)_{(o)}}{(UO_2)_{(aq)}} \qquad (2)$$

The values of D_o and K_{ext} for eqn (1) are given in Table 1

In the presence of complexing buffer anions and at the pH values of our experiments, complexation and/or hydrolysis can interfere with the extraction Under those conditions, the extraction constant is written as

$$D_1 = \frac{[UO_2]_{(o)}}{[UO_2]_{(aq)} + [UO_2(OH)_n]_{(aq)} + [UO_2X_m]_{(aq)}} = \frac{D_o}{1 + \beta_n[OH]^n + \beta_m[X]^m} \qquad (3)$$

When humate is also present to complex the uranyl, this expression is modified to

$$D_2 = \frac{D_o}{1 + \beta_n[OH]^n + \beta_m[X]^m + \beta_p[Hu]^p} \qquad (4)$$

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Upon rearrangement and substitution, we obtain

$$D_o\left[\frac{1}{D_2}-\frac{1}{D_1}\right]=\beta_1[\mathrm{Hu}]+\beta_2[\mathrm{Hu}]^2 \qquad (5)$$

a plot of $(D_o/[\mathrm{Hu}])[(1/D_2)-(1/D_1)]$ vs [Hu] will give a straight line of intercept β_1 and zero slope if only a 1 1 complex is formed and one of intercept β_1 and slope of β_2 if a 1 2 complex is formed

D_o is obtained by extrapolation of the extraction constant measured below pH 3 in the absence of buffer to the value for the pH of the humate experiments as this eliminated hydrolysis[9] and complexing D_1 is measured at the pH and buffer concentration of the humate experiments but in the absence of the latter reagent A pH range of 3–4 2 was used to ensure solubility of the humic acid while minimizing hydrolysis Glycolic acid was chosen as the buffer for these experiments as the acetic acid used in the earlier studies was not sufficiently effective at the lower pH values The humate concentration in eqn (1) was calculated from the appropriate degree of ionization for the pH of the experiment A typical set of extraction data are presented in Table 2 Table 3 presents the results of the temperature measurements Table 4 lists the calculated values of β_1 and β_2 and the thermodynamic parameters obtained from

Table 1 Uranyl extraction data

Organic phase 10 ml 10^{-4} M $(HDEHP)_2$ solution in tolune

Aqueous phase 10 ml 0 09 M $NaClO_4$ + 0 01 M glycolic acid

T	pH	D_o	log K_{ext}	$\frac{1000}{T}$
275 25	3 076	10 44	2 867	3 633
		10 45	2 867	
282 05	3 081	8 95	2 790	3 545
		9 14	2 799	
289 75	3 058	7 24	2 744	3 451
		7 32	2 749	
296 05	3 092	6 20	2 608	3 355
		6 36	2 613	
307 25	3 105	5 58	2 537	3 255
		5 54	2 534	

Table 2 Uranium(VI) humate binding

Organic phase 10 ml 10^{-5} M $(HDEHP)_2$ solution in toluene

Aqueous phase 10 ml 0 09 M $NaClO_4$ + 0 01 M glycolic acid

pH = 4 04 D_o = 4 94 T = 298 1°K

humate (μeq/l)	Activity (org)	Activity (aq)	D_2	$\frac{D_o}{[Hu]}\left[\frac{1}{D_2}-\frac{1}{D_1}\right]\times 10^{-4}$
0 0	53500	40009	1 337	——
	54747	40356	1 351	——
31 6	34852	60946	0 572	15 7
	35429	61286	0 578	15 4
47 4	28988	69320	0 418	17 2
	28905	69400	0 416	17 3
63 2	24567	75560	0 325	18 2
	24568	75949	0 325	18 2
79 0	20956	81872	0 256	19 8
	20917	81746	0 256	19 8

Table 3 Effect of temperature on uranium(VI)—humate binding

$I = 0\ 09\ M\ NaClO_4 + 0\ 01\ M\ HGl$, pH = 4 04 ± 01($\alpha$ = 0 47)

T (^oK)	$\frac{1000}{T}$	log β_1	log β_2
275 25	3 633	5.13 ± 0 02	8 97 ± 0 03
282 05	3 545	5 14 ± 0 02	8 85 ± 0 03
289 75	3 451	5 11 ± 0 02	8 87 ± 0 04
298 05	3 335	5 11 ± 0 02	8 94 ± 0 04
307 25	3 255	5 08 ± 0 02	9 11 ± 0 04

Table 4 Thermodynamic constants for uranium(VI)—humate binding

$I = 0\ 09\ M\ NaClO_4 + 0\ 01\ M\ HGl$, T = 298$^oK$ pH = 4 04(α = 0 47)

Species	log β_1	$\Delta G_1^{‡}$	$\Delta H_1^{‡}$	ΔS_1^{+}
$UO_2(Hu)$	5 11 ± 0 02	-29 2 ± 0 1	-2 7 ± 0 4	89
$UO_2(Hu)_2$	8 94 ± 0 03	-51 0 ± 0 2	+8 ± 4	200

‡ kJ eq^{-1}

+ J K^{-1}eq^{-1}

plots of log β_n vs 1/T The values in Table 4 differ from those listed in Ref [4] as the latter were based on preliminary experiments

Extraction of uranyl in the presence of humate was studied for 0 005, 0 010 and 0 050 M glycolic acid at pH 4 1 The variation in D_1 corresponded well with the expected complexation based on the stability constant[10] for the 1 1 uranyl glycolate complex and indicated that hydrolysis played a minor role compared to complexation

DISCUSSION

Previous studies[2, 3] have shown that Am(III) and Th(IV) form 1 1 and 1 2 complexes with humate whereas Ca(II) forms only a 1 1 complex[1] UO_2^{+2} also forms 1 1 and 1 2 which is not unexpected as it typically forms complexes slightly stronger than trivalent actinides The thermodynamic data in Table 4 leads to the same conclusion as similar data for Ca(II) and Th(IV) binding to humate The strength of binding of these hard acid cations is due primarily to large, positive entropy terms which can be related to the dehydration of the cation and of humate which occurs with complexation

Our results with Ca(II), Am(III), UO_2^{+2} and Th(IV) would be most simply interpreted as indicating that these cations bind to the carboxylate sites in humic acids Many other potential donor sites are reported to be present but we find no basis to assume that they are active in binding hard acid cations A recent infrared study[11] of the binding of uranyl by coal humic acids has been interpreted as reflecting complexation of the UO_2^{+2} cations by carboxylate groups acting as bidentate ligands

The values in Table 4 can be used to estimate the effect of humic substances on uranyl behavior in natural ecosystems Szalay[11] had suggested as early as 1952 that humic acid is responsible for the geochemical enrichment of uranium in bioliths Szalay reported sorption of UO_2^{+2} by humic material as an ion exchange process with adsorption isotherms corresponding to the Langmuir equation This has been confirmed by other workers, e g [6 12] This indicates that humate binding of uranyl can compete with hydrolysis and carbonate complexation Uptake of uranium from sea water by the humic acid in brown coal[11] is further evidence of the relative strength of the humate complexes Using the value of the first hydrolysis constant from Baes and Mesmer[13] and estimating a value for the formation of $UO_2(OH)_2$ (we ignore polynuclear complexes in systems of trace level concentrations, i e $[UO_2^{+2}] \leq 1 \times 10^{-8}$ M) leads to $\beta_1^{OH} = 2 \times 10^8$ and $\beta_2^{OH} = 5 \times 10^{15}$ For a seawater pH of 8, values of log $\beta_1^{Hu} \sim 7\ 6$ and log $\beta_2^{Hu} \sim 11\ 5$ and dissolved humic acid concentration of 10^{-5} eq /l we obtain estimates of 60% $UO_2(OH)_2$ and 40% $UO_2(Hu)_{1,2}$ complex For pH 8 and 10^{-4} eq /l humic acid, the $UO_2(Hu)_{1,2}$ is > 98% The organic content of fresh and ocean waters is reported to correspond to this range of humic concentrations[14] However, when carbonate complexation is included at pH 8 with $[CO_3^{-2}] \approx 10^{-5}$ M ($\beta_2 = 10^{17.1}$, $\beta_3 = 10^{21.4}$), the uranyl is calculated to exist completely as the carbonate complexes Therefore in the ocean, we would predict that humate (and fulvate) cannot compete with carbonate as a complexor of uranyl

In natural waters of lower pH, this may not be the case For example, if the pH is 6, $[CO_3^{-2}] \sim 10^{-7}$ M, and the humate concentration 10^{-4} eqn (1), the uranyl will be complexed predominantly by humate Moreover, passage of ground water through insoluble humate-containing material would lead to strong sorption of the uranyl in the soil

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